Methods for the Examination of Waters and Associated Materials

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The Determination of Gross Alpha and Beta Radiation in Potable and Raw Waters by Rapid Screening Measurement with Gas Proportional Counting Detection

2024

The Determination of Gross Alpha and Beta Radiation in Potable and Raw Waters by Rapid Screening Measurement with Gas Proportional Counting Detection.

This booklet contains a method for the preparation of samples for rapid screening measurement of gross alpha and gross beta radioactivity in waters prior to subsequent analysis by gas proportional counting.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

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Contents

About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, wastewater and effluents as well as sewage sludges and biota.

In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors), systematic error (bias), total standard deviation and limit of detection - often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Committee of Analysts

The preparation of booklets within the series “Methods for the Examination of Waters and Associated Materials” and their continuing revision is the responsibility of the Standing Committee of Analysts (SCA) - Established 1972 by the Department of the Environment.

At present, there are several working groups, each responsible for one section or aspect of water quality analysis:

1. General principles of sampling and accuracy of results
2. Microbiological methods
3. Inorganic and physical methods, metals and metalloids
4. Organic methods
5. Biological, biodegradability and inhibition methods
6. Radiochemistry methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will appear on our website – the library for which serves as a record of the bona fide methods developed and produced by the Standing Committee of Analysts.

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Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

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Users should ensure they are aware of the most recent version they seek.

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed, and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc. Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety.

These should be consulted and be readily accessible to all analysts. Amongst such resources are:

HSE: Information about health and safety at work

RSC: Laboratory best practices

The Determination of Gross Alpha and Beta Radiation in Potable and Raw Waters by Rapid Screening Measurement with Gas Proportional Counting Detection.

1 Introduction

In the event of a nuclear accident, terrorist attack or other deliberate attempt to contaminate the public water supply, Water Companies will need to rapidly ascertain the health and safety risk relating to radioactivity and to establish activity levels in order to comply with the current Water Supply Regulations and Directive (EU) 2020/2184 of the European Parliament and Council 16 December 2020 on the quality of water intended for human consumption.

Based on WHO guidelines for drinking water, the UK Water Industry has adopted 0.1 $Bq.L^{-1}$ for gross alpha and 1 $Bq.L^{-1}$ for gross beta as levels above which more detailed analysis would be required.

The safety levels for screening are largely based on data published by the National Radiological Protection Board (NRPB) and discussed by the Environment Agency [(1)].

The proposed screening levels for rapid analysis are 5 $Bq.L^{-1}$ for gross alpha and 30 $Bq.L^{-1}$ for gross beta. Further radiological examination will be required to determine and identify the radiochemical contamination.

The method described herein relates to the preparation stage for water samples prior to determination by gas proportional counter. It is a modified version of the “Blue Book” Measurement of Alpha and Beta Activity of Water and Sludge Samples published in 1986 [(2)]. Because of the increase in required detection limits it is practicable to use reduced volumes and ashing times to decrease sample preparation to approximately three hours.

The volumes and ashing times described have been demonstrated to achieve detection limits for gross alpha and beta below 1 $Bq.L^{-1}$

This method has been developed using both a Berthold LB770 10-Channel instrument and a Protean MPC 9604* for counting. The intention is that users refer to their own documentation for the subsequent counting of the samples for gross alpha and gross beta.

* Note: this book in no way endorses a particular instrument manufacturer or supplier, this is listed as a guide only to the configuration set up in the specific analytical sections to enhance understanding.

2 Performance characteristics of the method

2.1 Substances determined

Alpha emitting radionuclides which are not volatile at 350 °C and non-volatile β active radionuclides with β max energies >0.3 MeV

2.2 **Type of sample**

Raw and potable waters.

2.3 **Basis of method**

Sample is concentrated, sulfated and ignited at 350 ± 10 °C. A counting source is prepared from the dried dissolved solids and the gross alpha and beta activity measured using a gas flow proportional counting system.

2.4 **Limit of Detection**

The Limit of Detection has been calculated using 3 times the standard deviation (SD) of the lowest level spikes in each individual matrix. The example values quoted are for the highest calculated SD for all matrixes, see Appendix 1 for typical values from individual matrixes.

Alpha, $\alpha = 0.87$ $Bq.L^{-1}$
Beta, $\beta = 0.57$ $Bq.L^{-1}$

2.5 **Recovery**

The recoveries were determined from data produced by three laboratories and is summarised in Appendix 1, Method Performance Data.

3. Principle

3.1 The sample is evaporated almost to dryness, converted to the sulfate form and then ignited at 350 ºC. A portion of the residue is transferred to a planchette, and the alpha and beta activity measured by a suitable gas proportional counting instrument.

3.2 In order to reduce the analytical time the major variations from the “Blue Book” method are:-

I. Use of a smaller sample volume.
II. A reduction in ashing time.

These modifications are consistent with the accuracy and precision requirements for the quoted screening levels.

4. Interferences

Variations in source thickness will result in differing degrees of self-absorption of alpha particles. Such variations are minimised by taking a constant weight of residue. In this method a fixed amount of calcium sulfate is added to provide sufficient solids to cover the planchette to constant thickness.

5 Hazards/COSHH

Strict regulations set out in the Environmental Permitting (England and Wales) Regulations (2016), Environmental Authorisations (Scotland) Regulations (2018) and the Ionising Radiations Regulations (2017), cover the use of radioactive materials in laboratories. Ionising Radiations Regulations (2017) is enforced by the Health and Safety Executive (HSE). Environmental regulations are enforced by The Environment Agency (EA) in England and the Scottish Environment Protection Agency (SEPA) in Scotland. Advice and information on radiological protection is available from UK Health Security Agency who can advise on the safety of radiochemical substances and processes. Before proceeding with this method please refer to the relevant COSHH records and see also warning below on preparation of alpha standard sources.

6. Reagents

All reagents are analytical grade except where stated.

i. Concentrated sulfuric acid (d_{20} 1.84), equivalent to 95% v/v.
ii. Concentrated nitric acid (d_{20} 1.42), equivalent to 69% v/v.
iii. Volatile organic solvents – acetone or methanol
iv. Calcium sulfate
v. Deionised water
vi. Potassium chloride
vii. A suitable ^{241} Americium standard for alpha counting

7. Apparatus

In addition to normal laboratory glassware and apparatus the following may be required.

i. Calibrated Analytical Balance, reading to a minimum of 0.0001 g.
ii. Hotplates with controllable thermostat and suitable heating sources e.g., sand filled trays, infra-red lamps.
iii. Muffle furnace - capable of heating to 350 ± 10 ºC
iv. Evaporating basins capable of holding 100 mL sample
v. Pestle and mortar or suitable grinding equipment
vi. Stainless steel planchettes for use with counting equipment
vii. Gross alpha/beta counting instrumentation

8. Sample collection and preservation

Samples should be collected in clean plastic containers with a minimum volume of 1 litre. The container should be filled completely. Acidification of samples should be completed as soon as possible after sampling by the addition of 10 mL concentrated

nitric acid (d_{20} 1.42) for each litre of sample collected. Analysis should be carried out as soon as possible after collection.

9. Counting Standard for Alpha and Beta Activity Measurement

CAUTION: This procedure requires the preparation of a dry powder spiked with alpha emitting radionuclides. Accidental ingestion of radioactive particulates must be avoided, and the use of a simple closed cabinet glove box is recommended for the preparation of the spiked sources. Alternatively, a laboratory fume cupboard may be used provided the extract draught is not excessive and liable to disturb or carry fine powder particles into the air.

Information on preparing an Alpha and Beta standard is given below however "in house" methods should be referred to for standard preparation procedure, QC regime and blanks as appropriate.

9.1 Alpha Standard Preparation

9.1.1 A working alpha standard can be prepared by weighing a suitable amount of primary ^{241} Americium standard into a volumetric flask on a calibrated analytical balance.

9.1.2 Calculate the weight of primary 241 Americium standard needed to give the required activity of working alpha standard and fill the volumetric flask to the mark with 0.5 M Nitric Acid.

9.1.3 To make planchettes with the working alpha standard add enough dried calcium sulfate to a pre-weighed evaporating basin for the number of planchettes required.

9.1.4 Using an autopipette add the volume of working alpha standard required to give the activity needed for the recovered residue along with a suitable volume of nitric acid (d_{20} 1.42) and approximately 1mL of sulfuric acid (d_{20} 1.84).

9.1.5 Evaporate to dryness on a hotplate while stirring occasionally to dissolve the calcium sulfate.

9.1.6 Once dry ignite the evaporating basin in a muffle furnace at 350 ± 10 ºC for 30 minutes, cool and obtain a weight for the recovered residue.

9.1.7 Divide the activity of the working alpha standard added by the weight of recovered solid to determine the activity of residue in $Bq.g^{-1}$ and then determine the weight required to make a planchette with the activity needed for the standard.

9.1.8 Grind the residue with a pestle to produce a fine powder and disperse the determined weight evenly over a planchette with a few drops of solvent and allow to dry.

9.2 Beta Standard Preparation

9.2.1 A beta standard can be prepared directly for Potassium Chloride by drying a suitable amount at 110 ± 5 ºC for 1 hour ± 5 minutes.

9.2.2 Once cooled, grind the Potassium Chloride with a pestle to produce a fine powder and disperse the required weight evenly over a planchette with a few drops of solvent.

9.2.3 The beta activity of ^{40} Potassium in natural potassium is 27.4 $Bq.g^{-1}$. Hence in Potassium Chloride this value is 14.4 $Bq.g^{-1}$. This activity can be used to determine the amount of dried Potassium Chloride required to make planchette with a specific activity.

10. Sample Preparation Procedure

10.1 Transfer 100 ± 5 mL of sample into a pre-weighed evaporating basin.

10.2 Add 0.5 ± 0.1 mL of concentrated sulfuric acid (d_{20}, 1.84) into the evaporating basin.

10.3 Place the evaporating basin on a hotplate or other suitable heat source and evaporate the measured volume of sample carefully until no further fumes are evolved.

10.4 Transfer the evaporating basin and contents to a muffle furnace, pre-heated to 350 ± 10 ºC and ignite for 30 minutes. On removal allow to cool.

10.5 Weigh the evaporating basin and contents to ± 0.001 g and hence calculate the mass, M, of the ignited residue.

10.6 If the residue is not fine, grind in a pestle and mortar.

10.7 Weigh 10A mg of residue, where A cm^2 is the area of the counting surface, to four decimal places ±0.001 g and disperse on a planchette. If the recovery of dried residue is not sufficient to achieve the required weight, calcium sulfate can be added to the planchette.

10.8 Disperse the residue evenly over a planchette with a few drops of solvent and allow to dry.

11 Counting Stage

11.1 Immediately after drying the source start measuring the activity on the planchette.

It is envisaged that users will refer to their own documentation for counting procedures and result calculation.

This method has been optimised and validated in conjunction with both Berthold LB770 and Protean MPC 9604 Low Level Counters.

Clearly longer counting times can be employed to increase confidence levels or achieve lower LOD's if required.

The above preparation method has been validated for a minimum counting time of 30 minutes. This is the minimum time to achieve the quoted confidence at the screening levels.

12. References

1. National Compliance Assessment Service Technical Report. “Review of Alpha and Beta Blue Book Methods; Drinking Water Screening Levels.” EA, NCAS/TR/2002/003 Feb.2002

2. Measurement of Alpha and Beta Activity of Water and Sludge Samples. The Determination of Radon-222 and Radon-226. The Determination of Uranium (including General X-Ray Fluorescent Spectrometric Analysis) 1985-1986. Methods for the Examination of Waters and Associated Materials.

Appendix 1 – Method Performance Data

A.1.1 Gross Alpha Recovery Data

Laboratory	Sample (Bq.L^{-1})	Result (Bq.L-1)	Standard Deviation	% Recovery	Calculated LOD (Bq.L^{-1})
Scottish Water	Treated Soft Water (5)	5.41	0.69	108.1	
United Utilities	Treated Soft Water (5)	5.14	0.46	102.9	
United Utilities	LOD Soft (1)	1.22	0.26	121.6	0.78
Scottish Water	Treated Hard Water (5)	5.31	0.71	106.1	
South East Water	Treated Hard Water (5)	4.29	0.42	85.8	
Thames Water	Treated Hard Water (5)	5.00	0.88	100.0	
South East Water	LOD Hard (1)	1.04	0.11	104.0	0.33
Scottish Water	Untreated Surface (5)	4.75	0.6	95.0	
United Utilities	Untreated Surface (5)	5.22	0.65	104.4	
Scottish Water	LOD Surface (1)	1.18	0.29	117.99	0.87
Scottish Water	Untreated Ground (5)	4.71	0.78	94.14	
South East Water	Untreated Ground (5)	3.73	0.51	74.6	
Thames Water	Untreated Ground (5)	4.80	0.74	96.1	
South East Water	LOD Ground (1)	1.13	0.18	113.0	0.54

A1.2 Gross Beta Recovery Data

Laboratory	Sample (Bq.L^{-1})	Result (Bq.L-1)	Standard Deviation	% Recovery	Calculated LOD (Bq.L^{-1})
Scottish Water	Treated Soft Water (30)	29.68	1.37	98.9	
United Utilities	Treated Soft Water (30)	30.60	0.31	101.8	
United Utilities	LOD Soft (1)	1.08	0.09	108.0	0.27
Scottish Water	Treated Hard Water (30)	30.54	1.78	101.8	
South East Water	Treated Hard Water (30)	30.54	1.95	101.8	
Thames Water	Treated Hard Water (30)	31.15	2.11	103.8	
South East Water	LOD Hard (1)	1.09	0.13	109.0	0.39
Scottish Water	Untreated Surface (30)	30.14	1.38	100.5	
United Utilities	Untreated Surface (30)	30.90	0.79	103.0	
Scottish Water	LOD Surface (1)	0.97	0.19	97.3	0.57
Scottish Water	Untreated Ground (30)	29.29	0.76	97.6	
South East Water	Untreated Ground (30)	29.40	1.35	98.0	
Thames Water	Untreated Ground (30)	32.18	1.74	107.3	
South East Water	LOD Ground (1)	1.19	0.06	119.0	0.18

Appendix 2 – Proficiency Testing Data

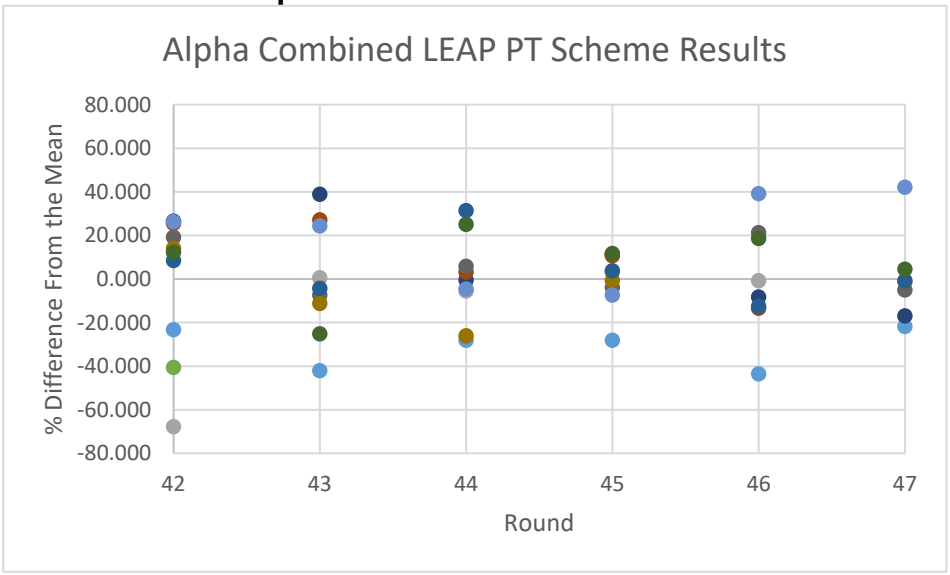
A.2.1 Summary

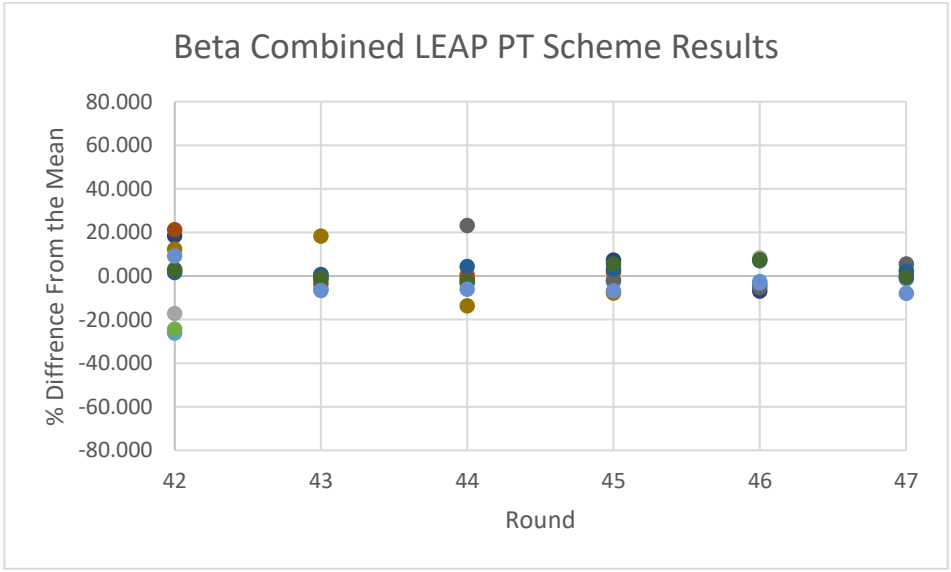
Proficiency test data is summarised in the table below. This data was acquired from 6 rounds of the LEAP proficiency testing scheme provided by FAPAS between 11/05/2021 and 03/10/2023.

A2.2 Results from FAPAS Drinking Water Chemical Contamination Proficiency Testing Scheme (LEAP)

Round	42		43		44		45		46		47	
Assigned Value (Bq.L-1)	α	β	α	β	α	β	α	β	α	β	α	β
	10.50	20.00	7.10	30.40	10.30	7.49	11.40	22.00	6.85	39.20	6.29	30.70
SEW	3.02	17.60	5.95	31.30	10.30	8.74	11.99	22.65	6.33	42.89	6.69	31.90
SWW	7.21	15.70	3.43	29.51	7.83	8.38	8.35	21.77	3.60	38.61	5.30	30.70
	5.59	16.07										
TW	11.90	25.20	8.22	30.89	10.85	8.52	12.94	23.99	5.85	36.87	5.63	31.10
	11.80	25.80	7.52	30.26	11.25	8.65	12.86	22.84	5.52	37.96		
SW	11.21	21.81	5.48	31.59	11.54	10.67	11.18	21.93	7.74	37.52	6.44	32.85
	10.72	23.88	5.25	37.11	8.06	7.47	11.54	20.60				
UU	10.20	21.59	5.66	31.55	14.33	9.03	12.06	23.07	5.58	42.41	6.73	31.81
	10.56	21.91	4.42	31.07	13.64	8.41	12.99	23.60	7.57	42.54	7.09	30.91
ALS	11.87	23.22	7.36	29.30	10.40	8.14	10.76	20.81	8.88	38.34	9.64	28.64
Mean	9.41	21.28	5.92	31.40	10.91	8.67	11.63	22.36	6.38	39.64	6.79	31.13
SD	3.076	3.6348	1.5436	2.2999	2.1762	0.8686	1.463	1.1747	1.6428	2.5167	1.4092	1.3195

A2.3 Combined Alpha and Beta Results from LEAP Scheme





Members assisting with these methods.

Without the good will and support given by these individuals and their respective organisations SCA would not be able to continue and produce the highly valued and respected blue book methods.

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Correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts:

secretary@standingcommitteeofanalysts.co.uk

Amendment History

The Determination of Gross Alpha and Beta Radiation in Potable and Raw Waters by Rapid Screening Measurement with Gas Proportional Counting Detection is a new book. Therefore, there isn't an amendment history in this occasion.

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